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Magnetic properties of $\text{Sr}_2\text{Ni}_{1-x}\text{Mg}_x\text{MoO}_6$ ($x = 0.25$ and 0.5) double perovskite structure

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Abstract. $\text{Sr}_2\text{Ni}_{1-x}\text{Mg}_x\text{MoO}_6$ ($x = 0.25$ and 0.5) double perovskites were synthesized by pyrolysis of glycerol–salt mixtures and their magnetic properties were investigated. X-ray diffraction was employed to refine crystal structures of these perovskite materials and set sample purity degree. The magnetic ground state of $\text{Sr}_2\text{Ni}_{1-x}\text{Mg}_x\text{MoO}_6$ ($x = 0.25$ and 0.5) has been characterized using magnetic susceptibility measurements. They indicate that $\text{Sr}_2\text{Ni}_{0.75}\text{Mg}_{0.25}\text{MoO}_6$ is ordered in an antiferromagnetic state below 56 K while $\text{Sr}_2\text{Ni}_{0.5}\text{Mg}_{0.5}\text{MoO}_6$ is paramagnetic.

1. Introduction

Complex oxides, which crystallize in the double perovskite structure, arouse the wide interest of researchers due to the large variety of electrical, magnetic, and catalytic properties. These compounds can be described by the general formula $A_2BB'O_6$, where A is an alkaline earth metal (Sr, Ca, Ba); B is 3d transition metal (Cr, Fe, Co, Ni, etc.) and B' is the diamagnetic hexavalent ion (Mo, W, Re, U) [1, 2]. Moreover, in the double perovskites, the B -sites are occupied by the magnetic B and the diamagnetic B' ions, alternatively.

The wide variety of $A_2BB'O_6$ compounds with different A , B , and B' ions shows various properties such as colossal magnetoresistance in $\text{Sr}_2\text{FeMoO}_6$ [3], half-metallicity in Sr_2CrWO_6 [4] and multiferroics in $\text{Sr}_2\text{NiMoO}_6$ [5, 6]. In a ground state, compounds based on Sr_2BMoO_6 ($B = \text{Ni, Co, Fe, Mn}$) crystallize in a tetragonal structure (space group $I4/m$), and a phase transition to a cubic structure occurs (space group $Fm-3m$) above room temperature. For example, in the $\text{Sr}_2\text{CoMoO}_6$ compound, the structural phase transition takes a place at temperature 560 K [7]. Partial or complete substitution of 3d



transition (Ni, Co, Fe, Mn) metals enables changing the temperature of both structural and magnetic phase transitions purposefully.

$\text{Sr}_2\text{NiMoO}_6$ double perovskite and derived compounds are intensively studied systems [5]. They have a number of physical and chemical properties that open up the prospect of their widespread use and for fundamental studies. First, double-perovskite-based compounds are considered as the basis for the anode of solid oxide fuel cells (SOFC). SOFC are promising electrochemical devices that convert chemical energy of fuel into electrical energy, with a high degree of energy conversion. Other advantages of SOFC are lack of noise, and low levels of environmental pollution [8]. Partial substitution of Sm^{3+} and Ba^{2+} [9] for Sr in $\text{Sr}_2\text{NiMoO}_{6-\delta}$ can improve the electrical conductivity but deteriorates the structural stability under oxidizing conditions. Doping of $\text{Sr}_2\text{NiMoO}_6$ by Mg allows to create the thermodynamically stable material possessing the high electrical conductivity and chemical and thermal compatibility with the Sr, Mg-doped lanthanum gallate electrolyte [10].

Moreover, the $\text{Sr}_2\text{NiMoO}_6$ -based compounds reveal multiferroic properties [5, 6], opening up broad technological applications for magnetic field sensors [11], recording and storing information, as well as in spintronics. $\text{Sr}_2\text{NiMoO}_6$ is the *B*-ordered double perovskite in which the magnetic Ni^{2+} ion resides on the *B* site and hexavalent diamagnetic Mo^{6+} ion occupies the *B'* locations. Its crystalline structure at room temperature is tetragonal and transforms to the cubic symmetry above 550 K [5].

The aim of this study is to study the effects of the partial substitution of Ni by Mg on the crystal structure and magnetic properties of $\text{Sr}_2\text{Ni}_{1-x}\text{Mg}_x\text{MoO}_6$ ($x = 0.25$ and 0.5).

2. Experimental details

The polycrystalline $\text{Sr}_2\text{Ni}_{1-x}\text{Mg}_x\text{MoO}_6$ samples ($x = 0.25$ and 0.5) were synthesized via the pyrolysis of glycerol-salt solutions with the addition of ammonium nitrate as a process combustion activator. The stoichiometric amounts of magnesium oxide MgO, nickel acetate $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, and strontium carbonate SrCO_3 with purity not less than 99.5 % were dissolved in dilute nitric acid HNO_3 . The resulting solution was transferred to a porcelain dish, and then the previously prepared solution of ammonium heptamolybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 2\text{H}_2\text{O}$ in distilled water was added. The solution containing the salts of the starting metals was kept at 353 K for 6 hours to ensure the mixing of metal cations at the molecular level. The ammonium nitrate NH_4NO_3 as a compound with the high exothermal effect and glycerol as an organic fuel (in the mass proportion 3:10) were added to the resulting solution. The resulting mixtures were heated on the plate to the auto combustion and dryness. The powders were annealed in air progressively at temperatures of 1173, 1273, and 1373 K for 24 hours with intermediate milling in ethanol. The heating/cooling rate of the furnace was 200 deg/hour. At the final stage, the samples were quenched from $T = 1373$ K down to room temperature at a rate of 300 deg/min.

The samples crystalline structure was determined using BRUKER D8 Advance high-resolution X-ray diffractometer and Inel Equinox 3000 using a Bragg-Brentano geometry with a Cu $K_{\alpha 1,2}$ source (wavelength $\lambda_1 = 1.540510$ Å and $\lambda_2 = 1.54422$ Å) at 298 K.

Neutron powder diffraction patterns were obtained at room temperature on the D2 diffractometer, at the WWR-2M reactor (Zarechny, Russia) (wavelength $\lambda = 1.805$ Å). Structural parameters were refined by Rietveld method using Fullprof program [12].

Magnetic measurements were performed with the Magnetic Property Measurement System (MPMS XL-7) in the temperature range (2–300) K, under the applied magnetic field of 1 kOe, in the zero-field cooled (ZFC) and the field cooled (FC) modes. The (2–100) K and (100–300) K intervals were investigated with the step 1 and 2 K, respectively. The magnetization vs magnetic field curves were obtained for magnetic fields range ± 70 kOe at 2 K.

3. Results and discussion

3.1. Structural study

Figure 1 shows the X-ray diffraction patterns of $\text{Sr}_2\text{Ni}_{0.75}\text{Mg}_{0.25}\text{MoO}_6$ and $\text{Sr}_2\text{Ni}_{0.5}\text{Mg}_{0.5}\text{MoO}_6$ obtained at 298 K. According to X-ray diffraction analysis, $\text{Sr}_2\text{Ni}_{1-x}\text{Mg}_x\text{MoO}_6$ ($x = 0.25$ and 0.5) samples are single-phase with minimal amounts of SrMoO_4 and Sr_3MoO_6 impurities (not more than 4.4 wt. %). This result is a characteristic feature of the Sr_2MMoO_6 ($M = \text{Mg, Mn, Fe, Co, Ni}$) double perovskite phase composition [1]. According to the X-ray data, with an increase doping magnesium ions up to 50 %, samples with a lower content of impurities (about 1.4 wt. %) are obtained.

Refinement of the structural parameters of the $\text{Sr}_2\text{Ni}_{1-x}\text{Mg}_x\text{MoO}_6$ ($x = 0.25$ and 0.5) samples from powder X-ray diffraction data at 298 K made it possible to establish that all $\text{Sr}_2\text{Ni}_{1-x}\text{Mg}_x\text{MoO}_6$ ($x = 0.25$ and 0.5) oxides are described on the basis of a tetragonal cell (space group $I4/m$) isostructural to pure $\text{Sr}_2\text{NiMoO}_6$. Crystallographic data for compounds $\text{Sr}_2\text{Ni}_{1-x}\text{Mg}_x\text{MoO}_6$ ($x = 0.25$ and 0.5) are in good agreement with our previous work [13].

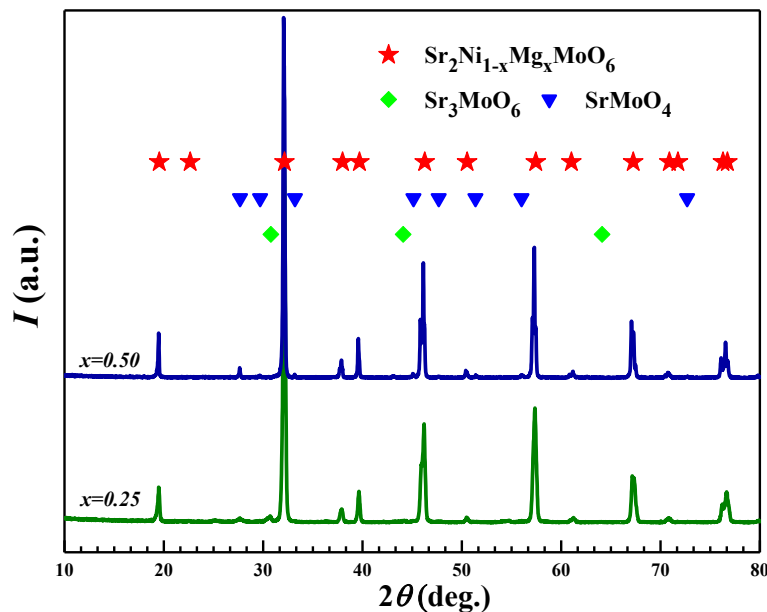


Figure 1. X-ray diffraction patterns of the $\text{Sr}_2\text{Ni}_{1-x}\text{Mg}_x\text{MoO}_6$ ($x = 0.25$ and 0.5) samples at room temperature.

As example, experimental and calculated X-ray $\text{Sr}_2\text{Ni}_{0.5}\text{Mg}_{0.5}\text{MoO}_6$ patterns are presented in figure 2. The unit cell parameters, atomic coordinates and agreement factors were calculated for the synthesized samples on the basis of a tetragonal ($I4/m$) are listed in Table 1. The best agreement between the experiment and the calculation is achieved with the following values of the structural parameters. Sr^+ ions occupy $4d$ position with coordinates $(0, 0.5, 0.25)$, $\text{Ni}^{2+}/\text{Mg}^{2+}$ ions occupy $2b$ position with coordinates $(0, 0.5, 0)$, Mo^{6+} ions are in position $2a$ $(0, 0, 0)$, and O^{2-} ions located at nodes $8h$ $(x, y, 0)$ and $4e$ $(0, 0, z)$.

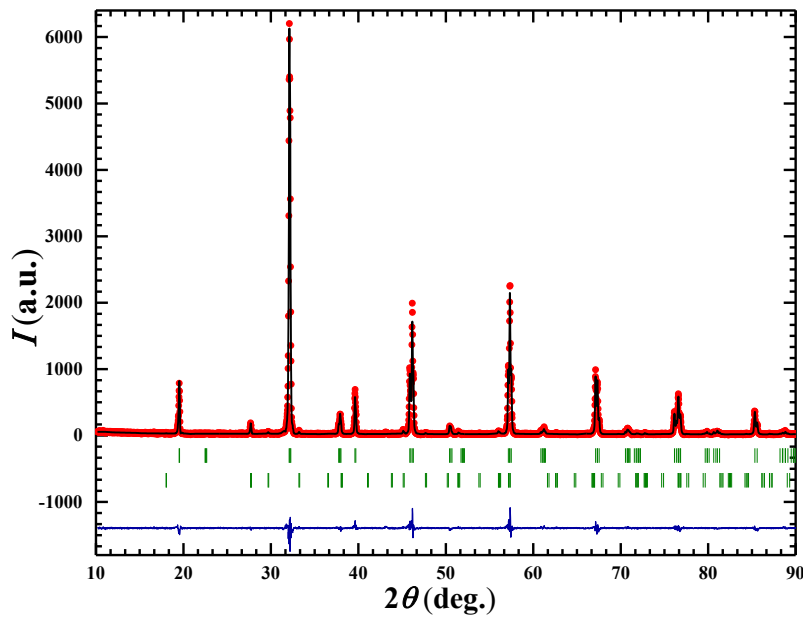


Figure 2. Observed (points) and calculated (line) XRD patterns of $\text{Sr}_2\text{Ni}_{0.5}\text{Mg}_{0.5}\text{MoO}_6$ at room temperature. The first row of the vertical bars is the Bragg reflection positions of the main phase; the second row – the impurity phase SrMoO_4 . The difference between calculated and observed intensities is shown at the bottom as solid line.

For the sample of $\text{Sr}_2\text{Ni}_{0.75}\text{Mg}_{0.25}\text{MoO}_6$ neutron diffraction measurements were performed. These data were used to determine the occupation coefficients of the positions of oxygen ions, as given in Table 1. The use of neutron diffraction is justified by the presence of light atoms, such as oxygen, whose position cannot be determined with X-ray diffraction with a high degree of confidence.

Table 1. A slightly more complex table with a narrow caption.

Parameter	$\text{Sr}_2\text{Ni}_{0.75}\text{Mg}_{0.25}\text{MoO}_6$	$\text{Sr}_2\text{Ni}_{0.5}\text{Mg}_{0.5}\text{MoO}_6$
a , Å	5.5471(1)	5.5568(2)
c , Å	7.8926(2)	7.9048(3)
V , Å ³	242.78(1)	244.08(1)
	Sr 4d (0, 1/2, 1/4)	
Occ (Sr)	0.232(3)	0.225(6)
	Ni(Mg) 2b (0, 0, 1/2)	
Occ (Ni)	0.089(1)	0.061(1)
Occ (Mg)	0.027(1)	0.061(1)
	Mo 2a (0, 0, 0)	
Occ (Sr)	0.114(1)	0.112(2)
	O1 8h (x, y, 0)	
x	0.272(2)	0.279(2)
y	0.206(2)	0.204(2)
Occ (O1)	0.498(2)	0.51(2)
	O2 4e (0, 0, z)	
z	0.239(2)	0.253(2)
Occ (O2)	0.252(1)	0.25(1)
R_f , %	2.79	4.30
χ^2 , %	2.99	4.19

As compared with undoped $\text{Sr}_2\text{NiMoO}_6$ the unit cell parameters of $\text{Sr}_2\text{Ni}_{1-x}\text{Mg}_x\text{MoO}_6$ rise with increasing magnesium concentration due to the size effect: the ionic radii of Ni^{2+} and Mg^{2+} are 0.69 and 0.72 Å, respectively [14]. The crystallographic data of $\text{Sr}_2\text{Ni}_{1-x}\text{Mg}_x\text{MoO}_6$ are in good agreement with our previous works [13, 15].

3.2. Magnetic properties

Figure 3 shows the temperature dependences of the molar susceptibility ($\chi_m(T)$) of $\text{Sr}_2\text{Ni}_{1-x}\text{Mg}_x\text{MoO}_6$ ($x = 0.25$ and 0.5) polycrystals measured in the ZFC-FC modes upon $H = 1$ kOe. As one can see from figure 3a, the $\text{Sr}_2\text{Ni}_{0.75}\text{Mg}_{0.25}\text{MoO}_6$ sample undergoes a second-order transition from the antiferromagnetic phase to paramagnetic state at Néel temperature $T_N = 56(1)$ K. Below 30 K there is an increase of molar susceptibility. This may be due to the presence of a very small amount of magnetic impurities (which were not detected according to X-ray data), the paramagnetic contribution of which increases with decreasing temperature. Nonlinearity in the magnetization curves at 2 K (see figure 4) in large fields is observed for both samples and is most likely associated with the magnetization of these impurities. Also, this may be due to the fact that individual isolated regions of disordered atoms remain, which follow the usual thermal dependence of paramagnetic substances [16]. The phase transition temperatures were determined from the temperature dependences of the first derivative of the susceptibility, similarly to Ref. [17]. In compare with pure $\text{Sr}_2\text{NiMoO}_6$ ($T_N = 82(1)$ K [5]) – the 25 at. % doping by Mg decreases the Néel temperature.

The doping 50 at. % by magnesium, the shape of the temperature dependence of molar susceptibility corresponds to the typical susceptibility curve of a paramagnetic (see figure 3b) [18]. This is due to the fact that high concentrations of magnesium ions in $\text{Sr}_2\text{Ni}_{1-x}\text{Mg}_x\text{MoO}_6$ destroy the magnetic order. This is also confirmed by the change in the shape of temperature dependence of the molar susceptibility (see figure 3).

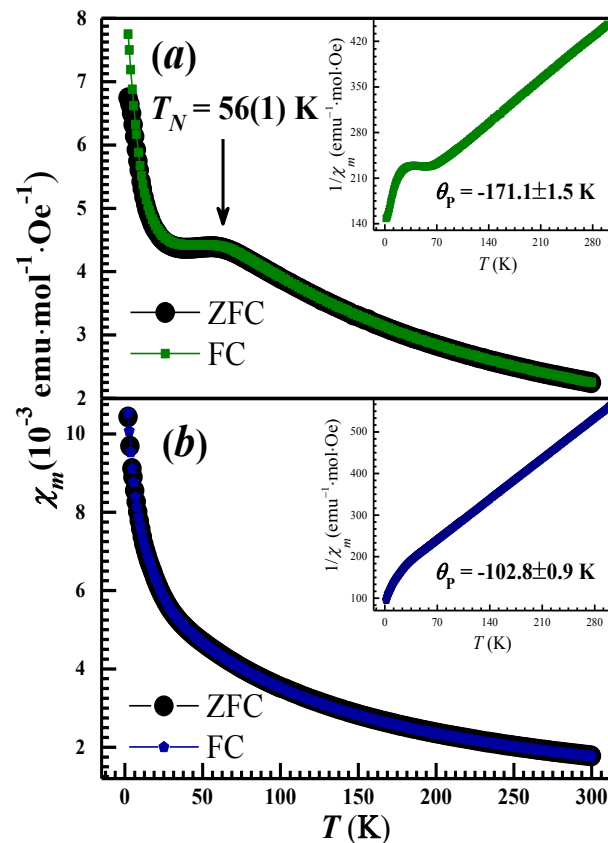


Figure 3. X-ray diffraction patterns of the $\text{Sr}_2\text{Ni}_{1-x}\text{Mg}_x\text{MoO}_6$ ($x = 0.25$ and 0.5) samples at room temperature.

The magnetization vs magnetic field curves measured at 2 K on the doping concentration Mg_x is given in figure 4. The magnetization curve as a function of a magnetic field for $\text{Sr}_2\text{Ni}_{0.75}\text{Mg}_{0.25}\text{MoO}_6$

displays almost linear behaviour at temperature of 2 K, which confirms the presence of antiferromagnetic ordering [16]. With increasing the concentration Mg_x the shape of the curve changes, which corresponds to a destroy of the magnetic order in the $Sr_2Ni_{0.5}Mg_{0.5}MoO_6$ sample and its transition to the paramagnetic state. This confirms the measurement data on the molar susceptibility of

$Sr_2Ni_{1-x}Mg_xMoO_6$ double perovskites.

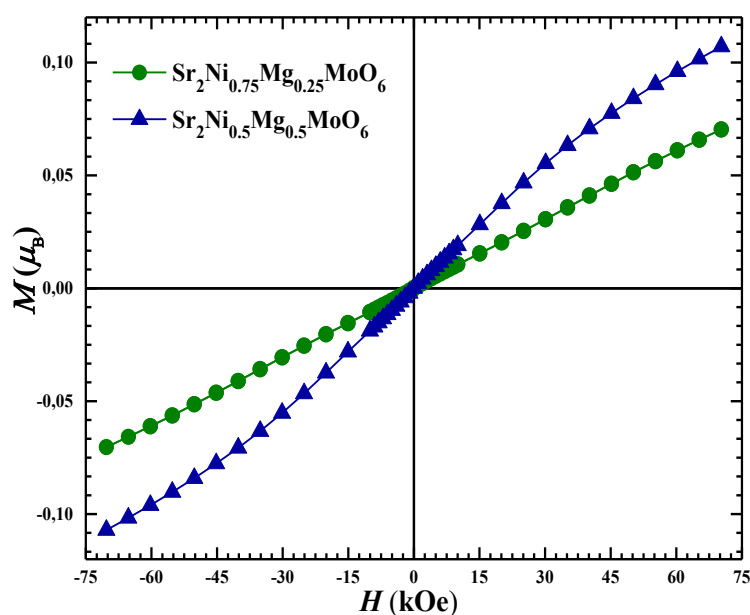


Figure 4. Magnetization versus magnetic field of $Sr_2Ni_{1-x}Mg_xMoO_6$ ($x = 0.25$ and 0.5) at 2 K measured under a magnetic fields range ± 70 kOe.

4. Conclusions

The polycrystalline $Sr_2Ni_{1-x}Mg_xMoO_6$ ($x = 0.25$ and 0.5) molybdates with the double perovskite type structure were obtained via the glycerol-salt precursors route with the addition of ammonium nitrate as a combustion activator. The structure of these perovskites has been studied with XRD. The polycrystals were described to have a tetragonal symmetry ($I4/m$).

Based on the measurement data on the magnetic susceptibility of $Sr_2Ni_{0.75}Mg_{0.25}MoO_6$, it is assumed that antiferromagnetic interactions are established at T_N around 56(1) K that lower Néel point of pure Sr_2NiMoO_6 .

The 50 at. % substituting for magnesium ions destroys the magnetic ordering, resulting to a paramagnetic state.

Acknowledgments

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References

- [1] Vasala S, Lehtimäki M, Huang Y H, Yamauchi H, Goodenough J B and Karppinen M 2010 *J. Solid State Chem.* **183** 1007
- [2] Rezaei N, Hashemifar T, Alaei M, Shahbazi F, Hashemifar S J and Akbarzadeh H 2019 *Phys. Rev. B* **99** 104411
- [3] Kimura T, Sawada H and Terakura K 1998 *Nature* **395** 677

- [4] Philipp J B, Majewski P, Alff L, Erb A, Gross R, Graf T, Brandt M S, Simon J, Walther T, Mader W, Topwal D and Sarma D D 2003 *Phys. Rev. B* **68** 144431
- [5] Eriksson A K, Eriksson S-G, Ivanov S A, Knee C S, Eriksen J, Rundlöf H and Tseggai M 2006 *Mater. Res. Bull.* **41** 144
- [6] Kumar S, Giovannetti G, van den Brink J and Picozzi S 2010 *Phys. Rev. B* **82** 134429
- [7] Ivanov S A, Eriksson S-G, Tellgren R, Rundlöf H and Tseggai M 2005 *Mat. Res. Bull.* **40** 840
- [8] Goodenough J B and Huang Y-H 2007 *J. Power Sources* **173** 1
- [9] Kumar P, Presto S, Sinha A S K, Varma S, Viviani M and Singh P 2017 *J. Alloys Compd.* **725** 1123
- [10] Filonova E A, Dmitriev A S, Pikalov P S, Medvedev D A and Pikalov E Y 2014 *Solid State Ionics* **262** 365
- [11] Cheong S-W and Mostovoy M 2007 *Nat. Mater.* **6** 13
- [12] Rodrigues-Carvajal J 1993 *Phys. B* **55** 192
- [13] Skutina L S, Vylkov A I, Grzhegorzhevskii K V, Chuikin A Yu, Ostroushko A A and Filonova E A 2017 *Inorg. Mater.* **53** 1293
- [14] Shannon R D and Prewitt C T 1969 *Acta Cryst.* **25** 925
- [15] Filonova E A, Russkikh O V, Skutina L S, Kochetova N A, Korona D V and Ostroushko A A 2018 *J. Alloys Compd.* **748** 671
- [16] Kayser P, Martínez-Lope M J, Alonso J A, Retuerto M, Croft M, Ignatov A and Fernandez-Díaz M T 2013 *Inorg. Chem.* **52** 11013
- [17] Kharchenko Yu N, Kharcheno N F, Baran M and Szymczak R 2003 *Low Temp. Phys.* **29** 579
- [18] Osinkin D A, Zabolotskaya E V, Kellerman D G and Suntsov A Yu 2018 *J. Solid State Electrochem.* **22** 1209